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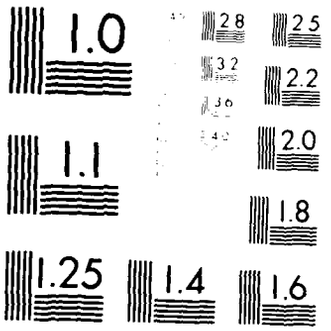

MICROCOPY RESOLUTION TEST CHART

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During the past two years a very substantial amount of progress has been made toward the main goal of this project, which is to calculate the activation energy of explosive molecules. The progress has come in the form of four different approaches to the problem: 1) CI method; 2) Gaussian 82 Computer Program; 3) MNDOC procedure; 4) Green's function techniques. We have recently obtained Dr. Henry F. Schaefer's CI programs, which are generally considered to be the best and fastest CI programs in the world. We have almost finished adapting these programs to the Cray computers, which are among the fastest computers in the world and are often referred to as super computers. When this adaptation is completed, we will have the first Cray version of Dr. Schaefer's CI programs, and in addition, we have access to several large Cray computers on which to run the programs. As a result, we expect to perform very large and highly accurate CI calculations on explosive molecules of interest. The new Cray version of these CI programs and the calculations that will be done with it are expected to arouse a very large amount of interest in the scientific community. The Gaussian 82 Computer Program is generally

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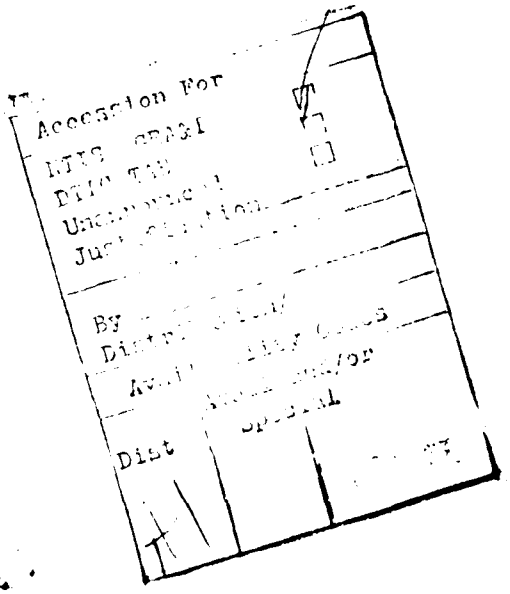
considered to be the state of the art program in the area of Moller-Plesset perturbation theory. We have recently obtained access to a new Cray version of Gaussian 82 which is not yet available to the general scientific community. With the combination of this new program and the large Cray computers to which we have access, we expect to perform activation energy calculations that are better and more accurate than those that were previously possible using Gaussian 82. The MNDOC method, which is a new correlated version of the MNDO method, has been used to compute accurate values for the activation energy of methyl nitrite. We have recently used Green's function theory to derive a new one-electron equation that goes beyond previous one-electron equations to include higher order correlation terms. As correlation plays a very important part in molecular reactions, this new equation is expected to lead to significant improvements in the calculation of molecular activation energies.



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Summary of Accomplishments

During the past two years, a very substantial amount of progress has been made toward the main goal of this project, which is to calculate the activation energy of explosive molecules. The progress has come in the form of four different approaches to the problem:

1) CI Calculations

It is well known that a full CI gives the best possible molecular total energies and activation energies that can be computed for a given basis set. However, since CI calculations can be very time-consuming, one must have very fast programs and very large computers in order to make the calculations feasible for explosive molecules of interest. We have recently obtained Dr. Henry F. Schaefer's CI programs, which are generally considered to be the best and fastest in the world. In addition, we have access to several large Cray computers, which are among the fastest in the world and are often referred to as super computers. We have almost finished converting Dr. Schaefer's CI programs to the Cray. Once we get these programs running on the Cray, we expect to perform very accurate CI calculations on many explosive molecules of interest. The new Cray version of these CI programs and the calculations that will be done with it are expected to arouse a large amount of interest in the scientific community.

2) Gaussian 82

The Gaussian 82 computer package is generally considered to be the "state of the art" program in the area of Moller-Plesset perturbation theory. This type of perturbation theory, if carried to high enough order, can yield very accurate results for molecular activation energies. We have very recently obtained access to a new Cray version

of Gaussian 82 which is not yet available to the general public. With the combination of this new program and the large Cray computers to which we have access, we expect to perform activation energy calculations that are better and more accurate than those that were previously possible using Gaussian 82.

3) MNDOC

The MNDOC method is a semi-empirical technique which is very fast and could therefore be used to compute the activation energies of large explosive molecules. One indication of MNDOC's potential is that it has yielded accurate values for the activation energy of methyl nitrite. Further improvements are needed in this method before it can be applied to a wide range of explosive molecules. We have recently discovered a modification that may greatly improve the method's accuracy. This modification consists of adding a two-configuration SCF to the MNDOC programs. The two-configuration SCF is expected to work well for molecules in which the ground state and first excited state are close in energy.

4) Green's Function Techniques

We have recently used Green's function theory to derive a new one-electron equation that goes beyond previous one-electron equations to include higher order correlation terms. As correlation plays a very important part in molecular reactions, this new equation is expected to lead to significant improvements in the calculation of molecular activation energies.

Introduction

The goal of this project is to calculate the amount of shocking or jostling that a solid explosive can withstand before detonating. The ultimate objective is to determine, by means of the calculations, how to modify the explosive so that it still retains all of its explosive power but becomes less sensitive to shock. These less sensitive but equally powerful explosives would reduce the number of accidents that occur among personnel involved in handling, storing, transporting, and using the explosives.

The detonation process is complicated and involves many factors, including "hot spots", propagation of acoustic or detonation waves, interaction (or scattering) between detonation waves and explosive molecules, etc. However, the key factor in an explosive's sensitivity to shock is the activation energy of the molecules that make up the explosive. When an explosive receives a shock, the energy of the molecules contained in the explosive is increased. In the region of the shock, if the energy of a sufficient number of molecules is raised above the activation energy, then the detonation begins. Thus if one can increase the activation energy, a bigger shock will be required for detonation and the explosive will be safer to handle. Therefore the first step in the study of detonations is to determine accurate values for the activation energy of the explosive molecules.

One can determine the activation energy of an explosive molecule by calculating the total energy of the molecule as a function of a reaction coordinate such as a bond length or bond angle. At the value of the reaction coordinate where the total energy goes through a maximum, dissociation, or detonation, occurs, and the activation energy is the difference between this maximum total energy and the total energy of the molecule in its equilibrium state. Thus in order to obtain accurate values for

molecular activation energies, one must be able to compute accurate values for molecular total energies.

It is well known that in order to obtain accurate and useful values for molecular total energies, it is essential to include correlation effects. We have thoroughly studied four different methods for including correlation in molecular calculations:

1) CI Method

2) Gaussian 82 Computer Program

3) MNDOC Procedure

4) Green's Function Techniques

Very substantial progress has been made in all four of these areas and they all show great promise for yielding accurate molecular activation energies. Each of these methods is described in detail below.

I. CI Method

As mentioned above, a very attractive feature of a full configuration interaction (CI) calculation is that it will yield the best possible molecular activation energy that can be computed for a given basis set. Often it is not necessary to carry the CI all the way to completion, but rather to converge the CI to whatever degree of accuracy one desires for the molecular activation energies. However, for explosive molecules of interest, an accurate converged CI can be very time-consuming and therefore one must have very fast computer programs and very fast computers in order to make the calculation feasible.

We have recently obtained Dr. Henry F. Schaefer's CI programs[1-10], which are generally considered to be the best and fastest in the world. In addition to acquiring these programs, we are at present making a major improvement in their usefulness by adapting them to the Cray computers, which are among the fastest computers in the world and are often referred to as super computers. When this adaptation is completed, we will have the first Cray version of Dr. Schaefer's CI programs, and in addition, we have access to several large Cray computers on which to run the programs. As a result, we expect to perform very accurate CI calculations on explosive molecules of interest. The new Cray version of these CI programs and the calculations that will be done with it are expected to arouse a very large amount of interest in the scientific community.

In addition to their speed, another important feature of Dr. Schaefer's CI programs is their ability to perform a two-configuration SCF and then do a CI from that. While the starting point for CI calculations is usually a single-configuration SCF, or Hartree-Fock calculation, sometimes the CI will converge significantly faster if the starting point is a two-configuration SCF. This is particularly true for molecules like nitromethane in which the

ground state and first excited state are close in energy, and may also be true for larger explosive molecules that contain the nitro group, such as nitrobenzene and trinitrotoluene (TNT). Thus the two-configuration SCF further increases the ability of Dr. Schaefer's programs to yield a converged CI for explosive molecules of interest.

We now give a brief description of the CI method[11,12]. The CI procedure is used to solve the time-independent, nonrelativistic, rigid-nuclei, electronic Schroedinger equation:

$$H\Psi = E\Psi \tag{1}$$

where the Hamiltonian H, in atomic units, is given by

$$H = V_{NN} + \sum_{\mu} h_{\mu} + \sum_{\mu<\nu} g_{\mu\nu} \tag{2}$$

$$V_{NN} = \sum_{A<B} \frac{Z_A Z_B}{r_{AB}} \tag{3}$$

$$h_{\mu} = -\nabla_{\mu}^2 - \sum_{A} \frac{Z_A}{r_{A\mu}} \tag{4}$$

$$g_{\mu\nu} = \frac{1}{r_{\mu\nu}} \quad . \tag{5}$$

Here the upper-case Latin subscripts represent the (rigid) nuclei, the lower-case Greek subscripts represent the electrons, the Z's are atomic numbers, and the r's (r_{AB}, $r_{A\mu}$, $r_{\mu\nu}$) are the distances between the particles. The V_{NN} term is a constant since the nuclei remain fixed, and therefore we can ignore it throughout the calculation.

In order to solve the Schroedinger equation, we write the wave function Ψ as a linear combination of symmetry adapted configuration functions Φ_s:

$$\Psi = \sum_{s} c_s \Phi_s \tag{6}$$

where the Φ_s's are linear combinations of Slater determinants. In a CI

calculation, one need include only configurations of the same symmetry as the particular electronic state being investigated (the reference state), since Hamiltonian matrix elements between configurations of different symmetry are zero. Hence the configuration functions are chosen to have the symmetry of the reference state. Since the total number of configurations of all symmetries can be very large, the symmetry adaptation of the configuration functions greatly reduces the size of the Hamiltonian matrix and simplifies the calculation.

The coefficients c_s are chosen to minimize the energy

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{7}$$

according to the variation principle. The variation principle ensures that the lowest calculated energy is an upper bound for the exact lowest eigenvalue of H (i.e., the exact ground state energy). It also ensures that the lowest calculated energy for each symmetry is an upper bound to the exact lowest eigenvalue of that particular symmetry. Thus if one is investigating an excited state which is the lowest of a particular symmetry type, one need not include any lower states in the same calculation.

Application of the variation principle leads to the well-known eigenvalue equation

$$\sum_t [H_{st} - ES_{st}]c_t = 0 \tag{8}$$

which is solved, by standard techniques, for the eigenvalues E and coefficients c_t. In the above equation, H_{st} and S_{st} are the Hamiltonian and overlap matrix elements, respectively, and are given by

$$H_{st} = \langle \Phi_s | H | \Phi_t \rangle \tag{9}$$

$$S_{st} = \langle \Phi_s | \Phi_t \rangle \quad . \tag{10}$$

The main computational step in a CI calculation is the evaluation of the Hamiltonian matrix elements H_{st}.

In order to construct the configuration functions and evaluate the matrix elements, one chooses a set of atomic basis functions χ_p. One then writes the atomic orbitals ϕ_i as a linear combination of the basis functions

$$\phi_i = \sum_p \chi_p U_{pi} \tag{11}$$

where the coefficients U_{pi} are determined by an SCF (self-consistent field) or similar calculation. The evaluation of the Hamiltonian matrix elements is greatly simplified if one chooses the atomic orbitals ϕ_i to be orthonormal. The Hamiltonian matrix elements are then given by

$$H_{st} = \sum_{ij} a_{ij}^{st} h_{ij} + \sum_{ijk\ell} b_{ijk\ell}^{st} g_{ijk\ell} \tag{12}$$

where

$$h_{ij} = \langle \phi_i(\vec{r}_1) | h_1 | \phi_j(\vec{r}_1) \rangle \tag{13}$$

$$g_{ijk\ell} = \langle \phi_i(\vec{r}_1) \phi_k(\vec{r}_2) | g_{12} | \phi_j(\vec{r}_1) \phi_\ell(\vec{r}_2) \rangle \tag{14}$$

and the coefficients a_{ij}^{st} and $b_{ijk\ell}^{st}$ are determined by a projective reduction calculation[13]. The integrals h_{ij} and $g_{ijk\ell}$, which are called orbital integrals, can be obtained from analogous basis set integrals, $\bar{h}_{ij}$ and $\bar{g}_{ijk\ell}$, by the transformation

$$h_{ij} = \sum_{pq} U_{pi}^* U_{qj} \bar{h}_{pq} \tag{15}$$

$$g_{ijk\ell} = \sum_{pqrs} U_{pi}^* U_{qj} U_{rk}^* U_{s\ell} \bar{g}_{pqrs} \tag{16}$$

where

$$\bar{h}_{pq} = \langle \chi_p(\vec{r}_1) | h_1 | \chi_q(\vec{r}_1) \rangle \tag{17}$$

$$\bar{g}_{pqrs} = \langle \chi_p(\vec{r}_1)\chi_r(\vec{r}_2)|g_{12}|\chi_q(\vec{r}_1)\chi_s(\vec{r}_2)\rangle \quad . \tag{18}$$

The transformation of the two-electron integrals, Eq. (16), can be quite time-consuming and must therefore be handled efficiently.

To summarize, the major computational steps in a CI calculation are the following:

1) Choose a basis set and compute the basis set integrals
2) Determine the orbitals by means of an SCF calculation
3) Transform the basis set integrals to orbital integrals
4) Choose and construct a set of symmetry adapted configuration functions for the electronic state that is being investigated
5) Calculate the Hamiltonian matrix elements with respect to the configuration functions
6) Compute the lowest eigenvalue(s) and eigenvector(s) of the Hamiltonian matrix

As mentioned previously, a full CI calculation (one in which all the configurations of a particular symmetry are included) yields the best possible total energy that can be computed for a given set of basis functions χ_p.

II. Gaussian 82 Computer Program

The Gaussian 82 computer program is the latest in a series of molecular orbital programs by John Pople and his group at Carnegie-Mellon University. Gaussian 82 is generally considered to be the "state of the art" program in the area of perturbation theory, and as such it has the potential to yield very accurate values for molecular activation energies. As in the case of the CI calculations discussed previously, the perturbation theory calculations can be very time-consuming and therefore very fast computers are needed to obtain accurate results for explosive molecules of interest. We have recently made substantial progress in this area by gaining access to a new Cray version of Gaussian 82 that is not yet available to the general public. In addition, we have access to several large Cray computers on which to run the program. With these facilities we expect to calculate activation energies that are better and more accurate than those that have previously been computed with the Gaussian 82 method.

One of the main features of Gaussian 82 is its capability to perform Moller-Plesset perturbation theory[14] calculations up to fourth order. This is a significant improvement over the previous version of the program, [illegible], which could carry Moller-Plesset perturbation calculations up to second order. For many molecules, fourth order Moller-Plesset perturbation theory yields a large part of the correlation energy and hence yields accurate activation energies. In addition, Gaussian 82 can perform coupled cluster[15] calculations up to second order. The coupled cluster method also has the capability to yield accurate activation energies for explosive molecules.

B. SECH Equation

Carrying out step 1) of the iterations, we put Σ_0 into Eq. (13). Then Eq. (13) becomes the one-electron Hartree equation:

$$[h(x)+V(x)]u_{0i}(x) = E_{0i}u_{0i}(x) \tag{17}$$

and G_0 is given, according to Eq. (12), by

$$G_0(x,x',\omega) = \sum_i \frac{u^*_{0i}(x')u_{0i}(x)}{\omega-E_{0i}} \quad . \tag{18}$$

Putting Σ_0 into Eq. (2), we obtain the corresponding zeroth order vertex function Γ_0:

$$\Gamma_0(12,3) = \delta(12)\delta(13) \quad . \tag{19}$$

Then putting Γ_0 and G_0 into Eq. (3), we obtain the zeroth order polarization

$$P_0(12) = -iG_0(12)G_0(21) \tag{20}$$

which, by Eqs. (4) and (5), yields the zeroth order dielectric function and screened interaction:

$$\epsilon_0(12) = \delta(12) - \int v(13)P_0(13)\delta(32)d(3) \tag{21}$$

$$W_0(12) = \int v(13)\epsilon_0^{-1}(32)d(3) \quad . \tag{22}$$

The above formula for the polarization, Eq. (20), is a well-known result called the random phase approximation (RPA)[GW-RPA], and ϵ_0 and W_0 are the RPA dielectric function and screened interaction:

$$P_{RPA}(12) \quad P_0(12) \tag{23}$$

$$\epsilon_{RPA}(12) \quad \epsilon_0(12) \tag{24}$$

Eqs. (1)-(5) can be iterated to obtain successively more accurate expressions for Σ, Γ and P as functionals of G. At each stage of the iterations, the Green's function is determined by Σ through Eqs. (12) and (13). We start the iterations by setting Σ equal to zero:

$$\Sigma_0 = 0 \quad . \tag{16}$$

The iterations are then carried out in the following sequence:

1) Σ_0 determines G_0 through Eqs. (12) and (13)

2) Σ_0 and G_0 determine Γ_0 through Eq. (2)

3) Γ_0 and G_0 determine P_0 through Eq. (3)

4) P_0 determines ε_0 and W_0 through Eqs. (4) and (5)

5) Γ_0 and W_0 determine Σ_1 and G_1 through Eqs. (1),(12) and (13) (i.e., Γ_0 and W_0 are substituted into Eq. (1) and then Eqs. (1),(12) and (13) are solved self-consistently for Σ_1 and G_1)

6) Σ_1 and G_1 determine Γ_1 through Eq. (2)

7) Γ_1 and G_1 determine P_1 through Eq. (3)

8) P_1 determines ε_1 and W_1 through Eqs. (4) and (5)

9) Γ_1 and W_1 determine Σ_2 and G_2 through Eqs. (1),(12) and (13) (i.e., Γ_1 and W_1 are substituted into Eq. (1) and then Eqs. (1),(12) and (13) are solved self-consistently for Σ_2 and G_2)

etc.

$$(1) = (x_1, t_1)$$

$$(1^+) = (x_1, t_1+\eta)$$

where x includes space and spin coordinates $(x) = (\vec{r},\zeta)$ and $\lim_{\eta\to 0}$ is understood.

The Green's function satisfies the equation

$$[\, i\frac{\partial}{\partial t_1} - h(x_1) - V(1)]G(12) - \int \Sigma(13)G(32)d(3) = \delta(12) \qquad (10)$$

where h is the kinetic energy plus the interaction of the electron with the nuclei, and V is the average potential:

$$V(1) = -i\int v(13)G(33^+)d(3) \quad . \qquad (11)$$

The Fourier transform of the Green's function with respect to time is given by

$$G(x,x',\omega) = \sum_i \frac{u_i^*(x')u_i(x)}{\omega - E_i} \qquad (12)$$

where ω is the frequency, and the amplitudes u_i and energies E_i satisfy the following equation (which is the Fourier transform of Eq. (10)):

$$[h(x)+V(x)]u_i(x) + \int \Sigma(x,x')u_i(x')dx' = E_i u_i(x) \qquad (13)$$

$$V(x) = \int v(\vec{r},\vec{r}')\rho(x')dx' \qquad (14)$$

$$\rho(x) = \sum_{i\ \mathrm{occ.}} u_i^*(x)u_i(x) \quad . \qquad (15)$$

If the self-energy Σ is independent of frequency, then the amplitudes and energies given by Eq. (13) are one-electron wave functions and energies, and one can work in the one-electron picture.

A. Green's Function Formalism

For a neutral system containing N electrons, one can use Green's function theory to obtain the following set of self-consistent equations[21-23] for the self-energy Σ, vertex function Γ, polarization P, dielectric function ε, and screened interaction W:

$$\Sigma(12) = i\int W(1^+3)G(14)\Gamma(42,3)d(34) \tag{1}$$

$$\Gamma(12,3) = \delta(12)\delta(13) + \int\frac{\delta\Sigma(12)}{\delta G(45)}\, G(46)\Gamma(67,3)G(75)d(4567) \tag{2}$$

$$P(12) = -i\int G(23)\Gamma(34,1)G(42)d(34) \tag{3}$$

$$\varepsilon(12) = \delta(12) - \int P(13)v(32)d(3) \tag{4}$$

$$W(12) = \int v(13)\varepsilon^{-1}(32)d(3) \tag{5}$$

where v is the bare instantaneous Coulomb interaction:

$$v(12) = v(\vec{r}_1,\vec{r}_2)\delta(t_1,t_2) \tag{6}$$

$$v(\vec{r}_1,\vec{r}_2) = \frac{e^2}{|\vec{r}_1-\vec{r}_2|}\ , \tag{7}$$

G is the one-electron Green's function:

$$G(12) = -i[\langle\psi(1)\psi^\dagger(2)\rangle\theta(t_1-t_2) - \langle\psi^\dagger(2)\psi(1)\rangle\theta(t_2-t_1)] \tag{8}$$

$$\theta(t_1-t_2) = \begin{cases} 1 & t_1>t_2 \\ 0 & t_1<t_2 \end{cases}\ , \tag{9}$$

e is the charge of an electron, ψ is the Heisenberg field operator, and the brackets $\langle\ \rangle$ indicate the ground state expectation value. In the above equations, we have used the notation

above is the screened interaction used in the expansion of the self-energy. This screened interaction greatly speeds up the convergence of the series for the self-energy.

The first term in the series for the self-energy leads to the screened exchange plus Coulomb hole (SECH) one-electron equation[21-23] which is solved self-consistently to obtain correlated molecular energies. The SECH equation has never been used before in molecular calculations and, as mentioned above, is expected to yield accurate values for molecular energies. The second term in the self-energy series leads to a new one-electron equation that goes beyond the SECH equation to include higher order correlation effects.[27] This new equation, which we have called the SECH2 equation, has never been used before in either molecular or solid state calculations. It is a completely new equation that contains even more correlation than the SECH equation and is therefore expected to produce significant improvements in the calculation of correlated molecular energies. The basic Green's function formalism, the SECH equation, and the SECH2 equation are described in detail in Sections A-C.

IV. Green's Function Techniques

We have developed a new formalism[21-27], based on Green's function theory, for including correlation in molecular calculations. To our knowledge, this approach has never been applied to molecules. In this new formalism, one uses Green's function theory to obtain a set of successively more accurate expressions for the self-energy, which contains all of the exchange and correlation effects. Using this new formalism, one can include correlation effects in a successively more accurate way, until one obtains the desired degree of accuracy for the molecular energies. In this process, new molecular one-electron equations will be developed.

One of the main advantages of this Green's function formalism over other perturbation type approaches is that the self-energy is expanded in powers of a screened interaction rather than a bare Coulomb interaction. The screening of the interaction greatly speeds up the convergence of the power series for the self-energy.

Using only the first term in this series for the self-energy, we obtained excellent results for solids.[21-23] The question is, can this Green's function method also be applied to smaller systems such as molecules? We now present very strong evidence that Green's function methods can be successfully applied to molecules. There is a very large literature on the use of Green's function approaches to calculate correlated molecular energies. References 28-85 refer to some of the authors who have successfully applied Green's function techniques to molecules. These papers, which are only a partial list of the large body of publications in this area, clearly show that Green's function approaches can be successfully applied to molecules.

Once again, it should be noted that what distinguishes the Green's function method of this proposal from the Green's function methods cited

is true, then including more excitations would increase the error produced by this inconsistency. This would explain why BWEN2, which has single, double, triple and quadruple excitations, gives worse results than BWEN1, which has only double excitations.

The BWEN method, which is fast and can thus be applied to relatively large molecules, yields good results for the activation energy of methyl nitrite. The results are not as good for nitromethane and thus some improvements are needed before the BWEN procedure can be generally applied to larger molecules. One possible improvement is the incorporation of a two-configuration SCF into the MNDO method. The two-configuration SCF, rather than a single-determinant SCF (HF), can then be used as the zero-order reference state and the starting point for excitations in the BWEN second-order perturbation treatment. The two-configuration SCF is expected to work well for molecules such as nitromethane, in which the ground state and first excited state are close in energy.

Reaction	Experiment[20]	MNDO/CI[19]	BWEN	BWEN1	BWEN2
$CH_3NO_2 \rightarrow CH_3 + NO_2$	59.0	46.5	48.2	35.8	29.1
Cis $CH_3ONO \rightarrow CH_3O + NO$	41.1	53.1	37.1	33.3	28.2
Trans $CH_3ONO \rightarrow CH_3O + NO$	41.1		38.1	33.0	27.3

Table I. Comparison of computed activation energies and experimental values. Activation energies are in kcal/mole.

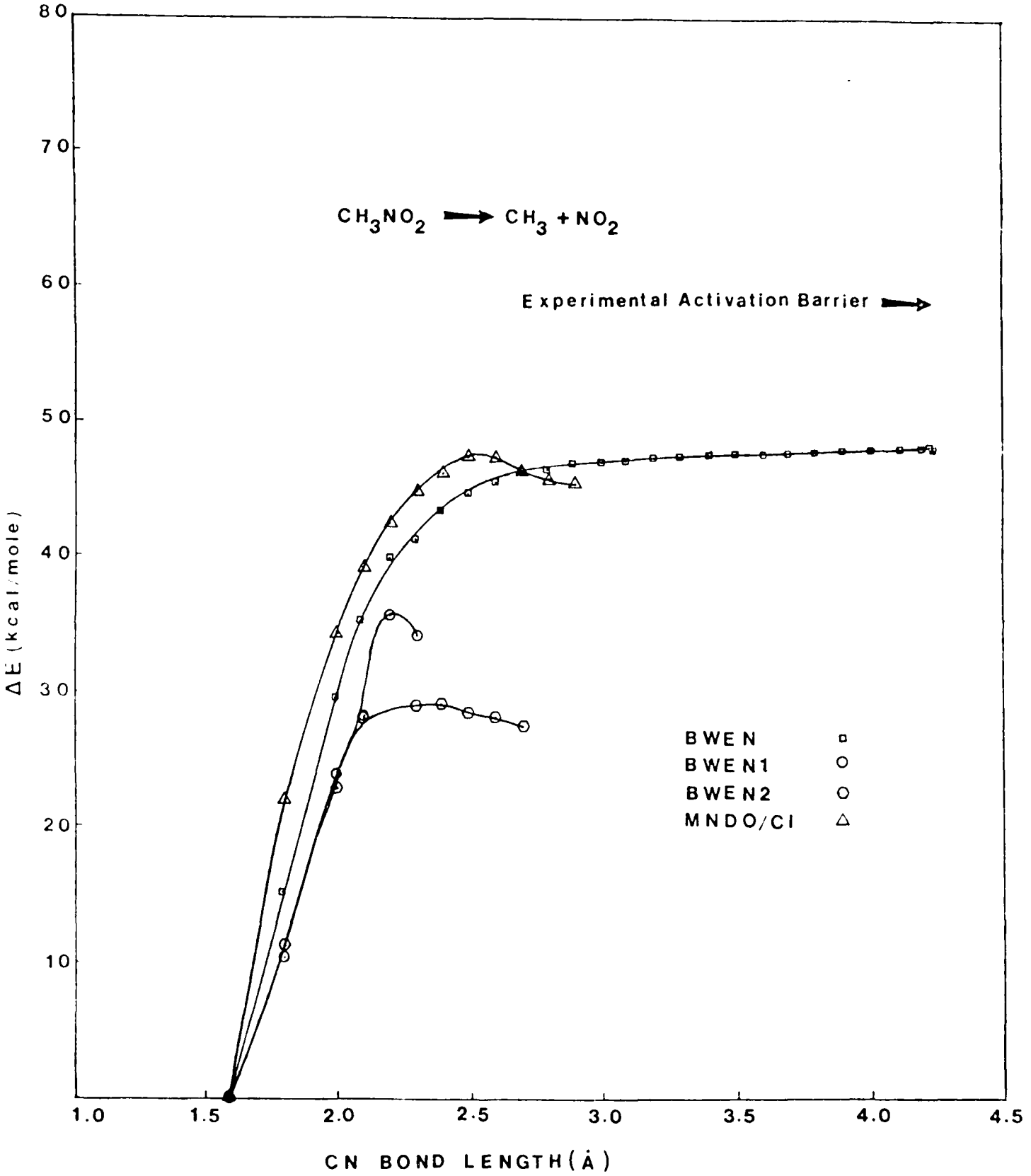

Figure 3. Computed reaction path curves for the dissociation of nitromethane. The arrow indicates the vertical position of the experimental activation energy.

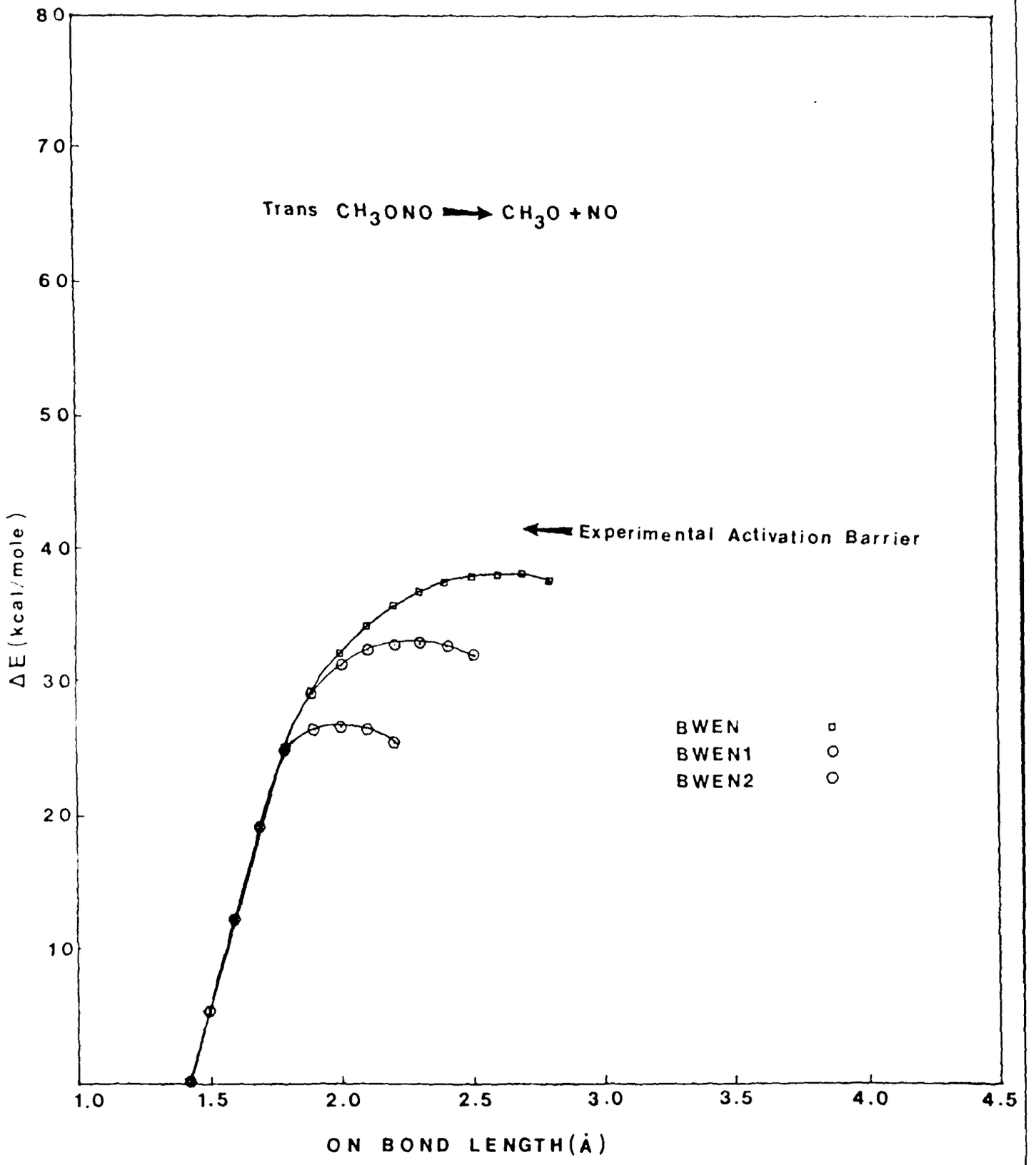

Figure 2. Computed reaction path curves for the dissociation of trans methyl nitrite. The arrow indicates the vertical position of the experimental activation energy.

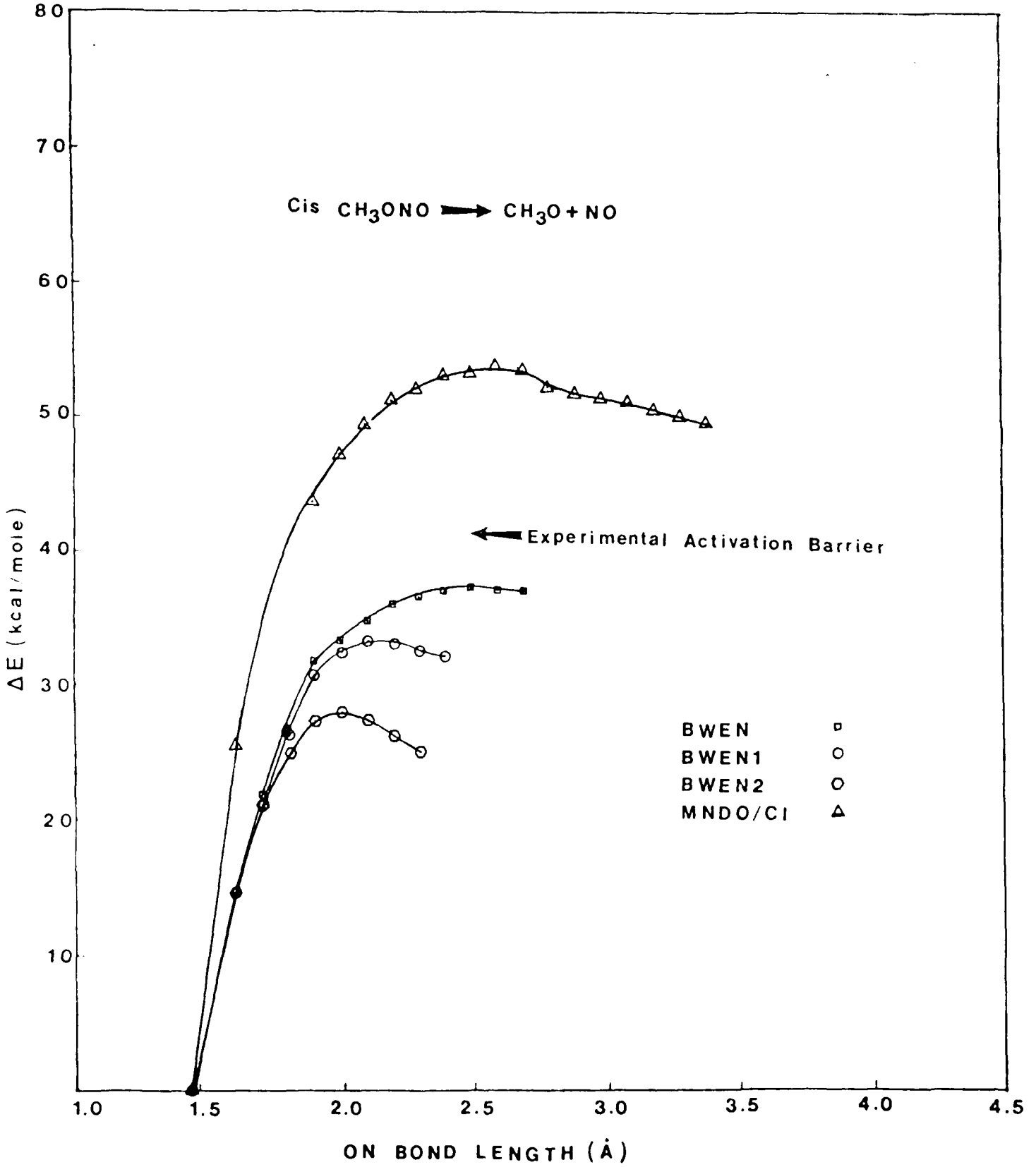

Figure 1. Computed reaction path curves for the dissociation of cis methyl nitrite. The arrow indicates the vertical position of the experimental activation energy.

compared these with Engelke's MNDO/CI results[19] and with experimental values. The MNDO/CI procedure used by Engelke is MNDO plus a minimal CI, where this minimal CI includes only the lowest double excitation. The calculated BWEN, BWEN1, and BWEN2 reaction path curves for the dissociation of CH_3ONO (cis and trans) and CH_3NO_2 are shown in Figs. 1-3, respectively. The MNDO/CI curves we calculated are shown for purposes of comparison. They are similar to the results Engelke obtained. Table I gives our computed BWEN, BWEN1, and BWEN2 activation energies and compares them with Engelke's MNDO/CI results and with experiment[20]. As shown by the table, the BWEN activation energy for CH_3NO_2 is within 11 kcal/mole of the experimental value and is only a slight improvement over the MNDO/CI result. For CH_3ONO, however, the BWEN calculation is a substantial improvement over the MNDO/CI result, giving activation energies that are within 4 kcal/mole and 3 kcal/mole of experiment for the cis and trans stereoisomers, respectively. Engelke calculated the MNDO/CI energy only for cis CH_3ONO. For both CH_3ONO and CH_3NO_2, the BWEN1 activation energies are not as close to experimental values as the BWEN results are, while the BWEN2 activation energies are even farther from experiment than the BWEN1 results. Thus for the activation energies of methyl nitrite and nitromethane, BWEN gives the best results. In both cases, these are improvements over the MNDO/CI results.

Since BWEN gives better results than BWEN1 and BWEN2 for the activation energies of CH_3ONO and CH_3NO_2, it appears that the procedure that works best for larger molecules is standard second-order perturbation theory in which the zero-order reference state is the HF ground state. When a different zero-order reference state (the lowest root of a two-configuration CI) is used but the excitations are still with respect to the HF ground state, as in BWEN1 and BWEN2, the results do not appear to be as good. This may be due to the inconsistency of using excitations from the HF ground state while using a zero-order reference state that is not the HF ground state. If this

over all states that are doubly excited with respect to the HF ground state. The MNDOC procedure also contains two variants of BWEN, called BWEN1 and BWEN2. In the BWEN1 method, the zero-order reference state for the second-order perturbation treatment is not the HF ground state but instead is the lowest root of a two-configuration CI matrix, where the two configurations are the HF ground state and the lowest doubly-excited state. The perturbation expansion then extends over all configurations that are doubly-excited with respect to the HF ground state. In the BWEN2 method, the zero-order reference state is again the lowest root of the two-configuration CI matrix mentioned above, but the perturbation expansion extends over single, double, triple and quadruple excitations with respect to the HF ground state. Since the BWEN2 perturbation expansion extends over a larger configuration space than BWEN1 does, BWEN2 is more time-consuming.

We considered the following reactions for the dissociation of CH_3NO_2 and CH_3ONO:

$$CH_3NO_2 \rightarrow CH_3 + NO_2$$

$$CH_3ONO \rightarrow CH_3O + NO$$

In these reactions, the dissociation releases highly reactive radicals that then attack whatever is available, releasing more energy than the bond breaking (or dissociation) required and thereby producing an explosion. In the case of methyl nitrite, we calculated the activation energy for dissociations proceeding from both the cis and trans configurations. As methyl nitrite probably contains both configurations, the dissociations could proceed either from both of them or from just one, with the other first converting to it.

For the three reactions shown above, we calculated the activation energies of the molecules using the BWEN, BWEN1 and BWEN2 procedures and

III. MNDOC Procedure

The MNDOC[16] method, which is a new correlated version of the MNDO[17] method, is a semi-empirical procedure for including correlation in calculations of molecular energies. One of the advantages of semi-empirical methods is that they are very fast. Due to its speed, the MNDOC method can be used to calculate potential surfaces, transition states, and activation energies of large explosive molecules. We have recently used the MNDOC method to calculate the activation energy of methyl nitrite (CH_3ONO) and nitromethane (CH_3NO_2).[18] In the case of methyl nitrite, the computed results were in good agreement with experiment, indicating that this fast method has the potential to yield accurate molecular activation energies. The nitromethane studies have suggested a modification of the MNDOC procedure which is expected to significantly increase its accuracy and thereby make it applicable to a wide range of explosive molecules. We have already begun work on this new modification, which is the incorporation of a two-configuration SCF into the MNDOC procedure. The two-configuration SCF is expected to work well for molecules like nitromethane in which there is a small energy separation between the ground state and first excited state. The two-configuration SCF is also expected to work well for larger explosive molecules that contain the nitro group, such as nitrobenzene and trinitrotoluene (TNT). The MNDOC method and results are described in more detail below.

Second-order perturbation theory, which is very fast, forms the basis of the MNDOC method. The MNDOC procedure uses Brillouin-Wigner perturbation theory with Epstein-Nesbet energy denominators (BWEN). In the BWEN method, the second-order perturbation theory is based on a single reference determinant: the Hartree-Fock (HF) ground state, and the perturbation expansion extends over

$$W_{RPA}(12) = W_0(12) \quad . \tag{25}$$

As shown by Eqs. (17), (18), (20), (21) and (24), the wave functions and energies that appear in the RPA formula for the dielectric function are Hartree wave functions and energies. Therefore one should use Hartree wave functions and energies to compute RPA dielectric functions.

Continuing the iterations with step 5), we put G_0 and W_0 into Eq. (1) to obtain the first order self-energy Σ_1 and first order Green's function G_1:

$$\Sigma_1(12) = i\int W_0(1^+3)G_1(14)\Gamma_0(42,3)d(34) \quad . \tag{26}$$

Using Eq. (18), Eq. (22) becomes

$$\Sigma_1(12) = iG_1(12)W_0(1^+2) \quad . \tag{27}$$

This expression for Σ_1 is the first term in the expansion of Σ in powers of the screened interaction W. The main point here is that we are expanding in a screened interaction rather than a bare Coulomb interaction. The screened interaction makes it possible to include more correlation while using fewer terms in the expansion (compared to the usual type of bare Coulomb interaction expansion).

If we want to work in the one-electron picture, we must obtain an expression for Σ_1 that is independent of frequency. We will then put this frequency-independent Σ_1 into Eq. (13) to obtain the one-electron wave functions u_{1i} and energies ε_{1i} that are used to define G_1 (according to Eq. (12)). In order to obtain a self-energy Σ_1 that is independent of frequency, we write the screened interaction W_0 as a bare Coulomb part plus a part W_0^P due to polarization:

$$W_0(1^+2) = v(1^+2) + W_0^P(1^+2) \quad . \tag{28}$$

It can be shown that $W_0^P(12)$ is a sharply peaked function of t_1-t_2. Therefore we will approximate W_0^P in Eq. (28) by its integrated value times a δ function; however, instead of $\delta(t_1-t_2+\eta)$ we will use $\delta(t_1-t_2)$ so as to pick up contributions from both parts of the Green's function[21-23]:

$$W_0^P(1^+2) = W_0^P(x_1,x_2,\omega=0)\delta(t_1-t_2) \quad . \tag{29}$$

Σ_1 then becomes the screened exchange plus Coulomb hole (SECH) expression for the self-energy[21-23], which contains both exchange and correlation:

$$\Sigma_{SECH}(x,x') = -\rho_1(x,x')W_0(x,x',\omega=0) + \frac{1}{2}\delta(x,x')[W_0(x,x',\omega=0)-v(\vec{r},\vec{r}')] \tag{30}$$

where

$$W_0(x,x',\omega=0) = v(\vec{r},\vec{r}') + W_0^P(x,x',\omega=0) \tag{31}$$

and ρ_1 is the density matrix computed with the wave functions u_{1i}:

$$\rho_1(x,x') = \sum_{i\ occ.} u_{1i}^*(x')u_{1i}(x) \quad . \tag{32}$$

According to Eq. (22), we can write W_0 in terms of ε_0:

$$W_0(x_1,x_2,\omega=0) = \int v(\vec{r}_1,\vec{r}_3)\varepsilon_0^{-1}(x_3,x_2,\omega=0)dx_3 \tag{33}$$

where $\varepsilon_0(x_1,x_2,\omega=0)$ is the static RPA dielectric function. As noted earlier, the RPA dielectric function corresponds to the Hartree equation and is calculated with Hartree wave functions and energies.

Putting Σ_{SECH}, which is independent of frequency, into Eq. (13), we obtain the SECH one-electron equation:

$$[h(x)+V(x)]u_{1i}(x) + \int \Sigma_{SECH}(x,x')u_{1i}(x')dx' = E_{1i}u_{1i}(x) \qquad (34)$$

which is solved self-consistently to obtain correlated wave functions and energies. During this self-consistent process, the screening function ε_0 remains constant (it is not recalculated each time with SECH wave functions and energies, but rather it is calculated once and for all with Hartree wave functions and energies). The SECH wave functions u_{1i} and SECH energies E_{1i} are used to define the first order Green's function G_1, according to Eq. (12):

$$G_1(x,x',\omega) = \sum_i \frac{u^*_{1i}(x')u_{1i}(x)}{\omega - E_{1i}} \quad . \qquad (35)$$

C. SECH2 Equation

Putting Σ_1 and G_1 into Eq. (2), we obtain an equation for the first order vertex function Γ_1:

$$\Gamma_1(12,3) = \delta(12)\delta(13) + \int \frac{\delta\Sigma_1(12)}{\delta G_1(45)} G_1(46)\Gamma_1(67,3)G_1(75)d(4567). \quad (36)$$

Then using Eq. (27) for Σ_1, Eq. (36) becomes

$$\Gamma_1(12,3) = \delta(12)\delta(13) + iW_0(1^+2)\int G_1(16)\Gamma_1(67,3)G_1(72)d(67). \quad (37)$$

Solving the above equation for Γ_1, we obtain an infinite power series in W_0:

$$\begin{aligned}\Gamma_1(12,3) = {} & \delta(12)\delta(13) + iW_0(1^+2)G_1(13)G_1(32) \\ & - W_0(1^+2)\int G_1(63)G_1(37)W_0(6^+7)G_1(16)G_1(72)d(67) \\ & - iW_0(1^+2)\int G_1(83)G_1(39)W_0(8^+9)G_1(68)G_1(97)W_0(6^+7)G_1(16)G_1(72)d(6789) \\ & + \ldots . \end{aligned} \quad (38)$$

This Γ_1 and Σ_1 explicitly satisfy the Ward identity. Putting Eq. (38) for Γ_1 into Eq. (3), we obtain the first order polarization P_1:

$$\begin{aligned}P_1(12) = {} & -iG_1(21)G_1(12) \\ & + \int G_1(51)G_1(16)W_0(5^+6)G_1(25)G_1(62)d(56) \\ & + i\int G_1(71)G_1(18)W_0(7^+8)G_1(57)G_1(86)W_0(5^+6)G_1(25)G_1(62)d(5678) \\ & - \int G_1(91)G_1(1,10)W_0(9^+10)G_1(79)G_1(10,8)W_0(7^+8)G_1(57)G_1(86)W_0(5^+6) \\ & \qquad \times G_1(25)G_1(62)d(5678910) \\ & + \ldots . \end{aligned} \quad (39)$$

The above expression for P_1, like Eq. (38) for Γ_1, is an infinite power series in W_0. Putting P_1 into Eq. (4), we obtain the corresponding first order dielectric function ε_1:

$$\varepsilon_1(12) = \delta(12) - \int P_1(13)v(32)d(3) \ . \tag{40}$$

Then putting ε_1 into Eq. (5), we obtain the first order screened interaction W_1:

$$W_1(12) = \int v(13)\varepsilon_1^{-1}(32)d(3) \ . \tag{41}$$

Since the above expression for P_1 goes beyond the RPA to include higher order correlation terms, we call it the generalized RPA (GRPA) polarization, and we call ε_1 and W_1 the GRPA dielectric function and GRPA screened interaction respectively:

$$P_{GRPA}(12) = P_1(12) \tag{42}$$

$$\varepsilon_{GRPA}(12) = \varepsilon_1(12) \tag{43}$$

$$W_{GRPA}(12) = W_1(12) \ . \tag{44}$$

According to Eqs. (39) and (42), the GRPA formula for the polarization contains both W_0 and G_1. As mentioned previously, W_0 is the RPA screened interaction and is computed with Hartree wave functions and energies, while G_1 is computed with SECH wave functions and energies, according to Eq. (35). Thus both Hartree wave functions and energies, and SECH wave functions and energies are used in the computation of P_{GRPA} and ε_{GRPA}.

Eq. (39) can be written as an integral equation if one defines the two-body polarization π by

$$\pi(1,2,3,4) = \pi_0(1,2,3,4) - \int \pi(5,2,3,6) W_0(5^+6) \pi_0(1,5,6,4) d(56) \quad (45)$$

where

$$\pi_0(1,2,3,4) = -iG_1(12)G_1(34) \quad . \quad (46)$$

Solving Eq. (45) for π yields

$$\begin{aligned}\pi(1,2,3,4) = \pi_0(1,2,3,4) &- \int \pi_0(5,2,3,6) W_0(5^+6) \pi_0(1,5,6,4) d(56) \\ &+ \int \pi_0(7,2,3,8) W_0(7^+8) \pi_0(5,7,8,6) W_0(5^+6) \pi_0(1,5,6,4) d(5678) \\ &- \int \pi_0(9,2,3,10) W_0(9^+10) \pi_0(7,9,10,8) W_0(7^+8) \pi_0(5,7,8,6) \\ &\qquad \times W_0(5^+6) \pi_0(1,5,6,4) d(5678910) \\ &+ \ldots . \end{aligned} \quad (47)$$

If one defines

$$P_1(12) \equiv \pi(2,1,1,2)$$

and uses Eq. (47), one obtains the following equation for P_1:

$$P_1(12) = \pi_0(2,1,1,2)$$

$$-\int \pi_0(5,1,1,6) W_0(5^+6) \pi_0(2,5,6,2) d(56)$$

$$+\int \pi_0(7,1,1,8) W_0(7^+8) \pi_0(5,7,8,6) W_0(5^+6) \pi_0(2,5,6,2) d(5678)$$

$$-\int \pi_0(9,1,1,10) W_0(9^+10) \pi_0(7,9,10,8) W_0(7^+8) \pi_0(5,7,8,6)$$

$$\times W_0(5^+6) \pi_0(2,5,6,2) d(5678910)$$

$$+ \ldots . \tag{49}$$

Then putting Eq. (46) for π_0 into Eq. (49), one obtains Eq. (39). Thus $P_1(12)$ is given by the integral equation (45) if one first solves Eq. (45) for π and then uses Eq. (48).

One can solve Eq. (45) for π in terms of inverses if one defines the inverses π^{-1}, π_0^{-1} and G_1^{-1} by

$$\int \pi(1,2,3,4) \pi^{-1}(4,6,5,1) d(14) = \delta(25)\delta(36) \tag{50}$$

$$\int \pi(1,2,3,4) \pi^{-1}(6,3,2,5) d(23) = \delta(15)\delta(46) \tag{51}$$

$$\int \pi(1,2,3,4) \pi^{-1}(4,6,2,5) d(24) = \delta(15)\delta(36) \tag{52}$$

$$\int \pi(1,2,3,4) \pi^{-1}(6,3,5,1) d(13) = \delta(25)\delta(46) \tag{53}$$

$$\pi_0^{-1}(1,2,3,4) = iG_1^{-1}(12) G_1^{-1}(34) \tag{54}$$

$$\int G_1(12) G_1^{-1}(23) d(2) = \delta(13) \tag{55}$$

$$\int G_1(12) G_1^{-1}(31) d(1) = \delta(23) \tag{56}$$

where, according to Eqs. (46) and (54)-(56),

$$\int \pi_0(1,2,3,4) \pi_0^{-1}(4,6,5,1) d(14) = \delta(25)\delta(36) \tag{57}$$

$$\int \pi_0(1,2,3,4)\pi_0^{-1}(6,3,2,5)d(23) = \delta(15)\delta(46) \tag{58}$$

$$\int \pi_0(1,2,3,4)\pi_0^{-1}(4,6,2,5)d(24) = \delta(15)\delta(36) \tag{59}$$

$$\int \pi_0(1,2,3,4)\pi_0^{-1}(6,3,5,1)d(13) = \delta(25)\delta(46) \quad . \tag{60}$$

Multiplying both sides of Eq. (45) by

$$\pi^{-1}(10,3,2,7)\pi_0^{-1}(4,9,8,1) \quad ,$$

integrating over coordinates 1,2,3 and 4, and then replacing coordinates 10,9,8,7 by 1,2,3,4 respectively, one obtains

$$\pi^{-1}(1,2,3,4) = \pi_0^{-1}(1,2,3,4) + W_0(3^+1)\delta(12)\delta(34) \quad . \tag{61}$$

Using Eq. (54) for π_0^{-1} , Eq. (61) becomes

$$\pi^{-1}(1,2,3,4) = G_1^{-1}(12)G_1^{-1}(34) + W_0(3^+1)\delta(12)\delta(34) \quad . \tag{62}$$

π is then given by

$$\pi(1,2,3,4) = [\pi^{-1}(1,2,3,4)]^{-1}$$

$$= [G_1^{-1}(12)G_1^{-1}(34) + W_0(3^+1)\delta(12)\delta(34)]^{-1} \tag{63}$$

where the inverse is defined by Eqs. (50) - (53). After $\pi(1,2,3,4)$ has been calculated from Eq. (63), $P_1(12)$ is then given by Eq. (48).

Continuing the iterations with step 9), we put P_1 and W_1 into Eq. (1) to determine G_2 and G_2:

$$\Sigma_2(12) = i\int W_1(1^+3)G_2(14)\Gamma_1(42,3)d(34). \qquad (64)$$

Putting Eq. (38) for Γ_1 into Eq. (64), we obtain an infinite series for Σ_2:

$$\begin{aligned}\Sigma_2(12) = {} & iG_2(12)W_1(1^+2) \\ & -\int G_2(14)W_1(1^+3)G_1(43)G_1(32)W_0(4^+2)d(34) \\ & -i\int G_2(14)W_1(1^+3)G_1(63)G_1(37)W_0(6^+7)G_1(46)G_1(72)W_0(4^+2)d(3467) \\ & +\int G_2(14)W_1(1^+3)G_1(83)G_1(39)W_0(8^+9)G_1(68)G_1(97)W_0(6^+7)G_1(46) \\ & \qquad \times G_1(72)W_0(4^+2)d(346789) \\ & + \ldots \end{aligned} \qquad (65)$$

We now define Σ_2' to be the first two terms in the above series:

$$\begin{aligned}\Sigma_2'(12) = {} & iG_2'(12)W_1(1^+2) \\ & -\int G_2'(14)W_1(1^+3)G_1(43)G_1(32)W_0(4^+2)d(34) \quad . \end{aligned} \qquad (66)$$

The above expression for Σ_2' is the first two terms in the expansion of Σ in powers of the screened interaction W, and G_2' is the corresponding Green's function. We will call Σ_2' the second order self-energy since it contains the first and second terms of the power series (it contains the W term and the W^2 term), and we will call G_2' the second order Green's function.

In order to continue working in the one-electron picture, we must obtain an expression for Σ_2' that is independent of frequency. We will then put this into Eq. (13) to obtain a new one-electron equation that contains higher order correlation terms. This new one-electron equation will yield correlated wave functions u_{2i} and correlated energies E_{2i} which, through Eq. (12), will yield

the second order Green's function G_2'. In order to obtain a frequency-independent expression for Σ_2', we treat the screened interactions that appear in Σ_2' (i.e., W_0 and W_1) in the same manner as W_0 was treated in the derivation of the SECH equation. In other words, W_0 and W_1 are written, according to Eq. (28), as a bare Coulomb part plus a part due to polarization:

$$W_0(4^+2) = v(4^+2) + W_0^P(4^+2) \tag{67}$$

$$W_1(1^+3) = v(1^+3) + W_1^P(1^+3) \quad . \tag{68}$$

Then we approximate W_0^P and W_1^P by their integrated value times a δ function:

$$W_0^P(4^+2) = W_0^P(x_4,x_2,\omega=0)\delta(t_4-t_2+\eta) \tag{69}$$

$$W_1^P(1^+3) = W_1^P(x_1,x_3,\omega=0)\delta(t_1-t_3+\eta) \quad . \tag{70}$$

In some cases, we remove the η from the δ functions in Eqs. (69) and (70) so as to pick up contributions from both parts of the Green's function, according to Eq. (29). In other cases, we retain the η in the δ functions in Eqs. (69) and (70) so as to pick up contributions from only one of the parts of the Green's function. Since each of the Green's functions in Eq. (66) has two parts (c.f. Eq. (8)), then the second term of Eq. (66) yields eight terms when Eq. (8) is substituted for G. By carefully considering the time dependence of the Green's functions in each of these terms and by using the appropriate δ functions in each case, we obtain the following frequency-independent expression for Σ_2', which we call Σ_{SECH2}:

$$\Sigma_{SECH2}(x_1,x_2) = -\rho_2(x_1,x_2)W_1(x_1,x_2,\omega=0)$$

$$+ \frac{1}{2}\,\delta(x_1,x_2)[W_1(x_1,x_2,\omega=0)-v(\vec{r}_1,\vec{r}_2)]$$

$$-\int\rho_2(x_1,x_4)W_1(x_1,x_3,\omega=0)\rho_1(x_4,x_3)\rho_1(x_3,x_2)W_0(x_4,x_2,\omega=0)dx_3dx_4$$

$$+ \frac{1}{2}\int\rho_2(x_1,x_4)W_1(x_1,x_3,\omega=0)\rho_1(x_4,x_3)\delta(x_3,x_2)[W_0(x_4,x_2,\omega=0)-v(\vec{r}_4,\vec{r}_2)]dx_3dx_4$$

$$+ \frac{1}{2}\int\delta(x_1,x_4)[W_1(x_1,x_3,\omega=0)-v(\vec{r}_1,\vec{r}_3)]\rho_1(x_4,x_3)\rho_1(x_3,x_2)W_0(x_4,x_2,\omega=0)dx_3dx_4$$

$$- \frac{1}{4}\int\delta(x_1,x_4)[W_1(x_1,x_3,\omega=0)-v(\vec{r}_1,\vec{r}_3)]\rho_1(x_4,x_3)\delta(x_3,x_2)[W_0(x_4,x_2,\omega=0)$$

$$-v(\vec{r}_4,\vec{r}_2)]dx_3dx_4 \qquad (71)$$

where ρ_2 is the density matrix computed with the wave functions u_{2i}:

$$\rho_2(x,x') = \sum_{i\ \text{occ.}} u^*_{2i}(x')u_{2i}(x) \quad . \qquad (72)$$

As shown by Eq. (71), Σ_{SECH} contains four higher order correlation terms (in addition to the screened exchange and Coulomb hole terms). The first of these higher order terms is the product of two screened exchanges, the second is the product of a screened exchange and a Coulomb hole, the third is the product of a Coulomb hole and a screened exchange, and the fourth is the product of two Coulomb holes. Thus Σ_{SECH2} is a natural second order extension of the screened exchange plus Coulomb hole self-energy Σ_{SECH}.

Putting Σ_{SECH2} into Eq. (13), we obtain a new one-electron equation that goes beyond the SECH equation to include higher order correlation terms:

$$[h(x)+V(x)]u_{2i}(x) + \int\Sigma_{SECH2}(x,x')u_{2i}(x')dx' = E_{2i}u_{2i}(x) \quad . \qquad (73)$$

We call this new equation the SECH2 equation. It is solved self-consistently to obtain wave functions u_{2i} and energies E_{2i} that have a high degree of correlation. During this self-consistent process, the screening functions

ε_0 and ε_1 remain constant (they are not recalculated each time with SECH2 wave functions and energies, but rather ε_0 is calculated once and for all with Hartree wave functions and energies, and ε_1 is calculated once and for all with SECH wave functions and energies). Also ρ_1 remains constant during the self-consistent process (ρ_1 is calculated once and for all with SECH wave functions). The only quantities that change during the self-consistent process are the SECH2 wave functions u_{2i} and the SECH2 energies E_{2i}.

The SECH2 equation is a new one-electron equation that has never been used before in either molecular or solid state calculations. It is expected to lead to substantial improvements in the calculation of correlated molecular energies.

References

1. R. R. Lucchese and H. F. Schaefer III, J. Am. Chem. Soc. 99, 6765 (1977).

2. S. Bell and H. F. Schaefer III, J. Chem. Phys. 67, 5173 (1977).

3. R. R. Lucchese and H. F. Schaefer III, J. Chem. Phys. 68, 769 (1978).

4. R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope and H. F. Schaefer III, J. Comp. Phys. 26, 243 (1978).

5. B. R. Brooks and H. F. Schaefer III, Int. J. Quant. Chem. 14, 603 (1978).

6. N. C. Handy, J. D. Goddard and H. F. Schaefer III, J. Chem. Phys. 71, 426 (1979).

7. Y. Yoshioka, J. D. Goddard and H. F. Schaefer III, J. Chem. Phys. 74, 1855 (1981).

8. Y. Osamura, Y. Yamaguchi and H. F. Schaefer III, J. Chem. Phys. 75, 2919 (1981).

9. Y. Osamura, Y. Yamaguchi and H. F. Schaefer III, J. Chem. Phys. 77, 383 (1982).

10. D. J. Fox, Y. Osamura, M. R. Hoffmann, J. F. Gaw, G. Fitzgerald, Y. Yamaguchi and H. F. Schaefer III, Chem. Phys. Lett. 102, 17 (1983).

11. H. F. Schaefer III, The Electronic Structure of Atoms and Molecules, (Addison-Wesley, Reading, Mass., 1972).

12. I. Shavitt, in Modern Theoretical Chemistry: Electronic Structure Theory, edited by H. F. Schaefer III, (Plenum Press, New York, 1977), Vol. 3, Chapter 6.

13. S. F. Boys and G. B. Cook, Rev. Mod. Phys. 32, 285 (1960).

14. C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).

15. G. D. Purvis III, R. Shepard, F. B. Brown and R. J. Bartlett, Int. J. Quant. Chem. 23, 835 (1983).

16. W. Thiel, J. Am. Chem. Soc. 103, 1413 1420 (1981).

17. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. 99, 4899 (1977).

18. L. M. Holaday, E. R. Hernandez, A. Bakhshai, R. H. Pressley and N. E. Brener, J. Chem. Phys. (submitted for publication).

19. R. Engelke, Chem. Phys. Lett. 83, 151 (1981).

20. S. W. Benson and H. E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, NSRDS NBS 21 (1980).

21. N. E. Brener and T. C. Collins, Proceedings of the Twelfth International Conference on the Physics of Semiconductors, (B. G. Teubner, Stuttgart, 1974), p. 174.

22. N. E. Brener, Phys. Rev. B11, 929 (1975).

23. N. E. Brener, Phys. Rev. B11, 1600 (1975).

24. N. E. Brener and J. L. Fry, Phys. Rev. B19, 1720 (1979).

25. N. E. Brener and J. L. Fry, Phys. Rev. B22, 2737 (1980).

26. N. E. Brener, J. L. Fry and T. C. Collins, Int. J. Quantum Chem. Symp. 14, 455 (1980).

27. N. E. Brener and A. Bakhshai, Phys. Rev. B (submitted for publication).

28. G. Y. Csanak, H. S. Taylor and R. Yaris, Adv. At. Mol. Phys. 7, 287 (1971).

29. J. D. Doll and W. P. Reinhardt, J. Chem. Phys. 57, 1169 (1972).

30. J. Ciczek and J. Paldus, Int. J. Quant. Chem. Symp. 6, 435 (1972).

31. J. Paldus and J. Ciczek, J. Chem. Phys. 60, 149 (1974).

32. B. T. Pickup and O. Goscinski, Mol. Phys. 26, 1013 (1973).

33. B. T. Pickup and O. Goscinski, Chem. Phys. Lett. 33, 265 (1975).

34. P. Jorgensen, Ann. Rev. Phys. Chem. 26, 359 (1975).

35. [illegible], Int. J. Quant. Chem. 9, 901 (1975).

36. [illegible], Chem. Phys. Lett. 36, 264 (1975).

37. [illegible] and Y. Öhrn, J. Chem. Phys. [illegible], 4063 (1974).

38. [illegible] and Y. Öhrn, J. Chem. Phys. 62, 2045 (1975).

39. [illegible] and Y. Öhrn, Chem. Phys. Lett. 33, 396 (1975).

40. [illegible] and Y. Öhrn, J. Chem. Phys. 65, 917 (1976).

41. [illegible] and W. T. Smith, J. Chem. Phys. 58, 4899 (1973).

42. [illegible], Chem. Phys. Lett. 25, 122 (1974).

43. [illegible], J. D. Smith and J. Simons, J. Chem. Phys. 61, 2670 (1974).

44. W. T. Smith, T. I. Chen and J. Simons, Chem. Phys. Lett. 26, 296 (1974).

45. [illegible] and J. Simons, J. Chem. Phys. 62, 535 (1975).

46. J. Kenney and J. Simons, J. Chem. Phys. 62, 592 (1975).

47. M. Griffing, J. Kenney, J. Simons and [illegible], J. Chem. Phys. 63, 4073 (1975).

48. P. Jorgensen and J. Simons, J. Chem. Phys. 63, 5302 (1975).

49. J. Simons and P. Jorgensen, J. Chem. Phys. 64, 1413 (1976).

50. K. Griffing and J. Simons, J. Chem. Phys. 64, 3610 (1976).

51. E. Anderson and J. Simons, J. Chem. Phys. 64, 4548 (1976).

52. K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Anderson and J. Simons, J. Chem. Phys. 64, 4730 (1976).

53. J. Simons and E. Dalgaard, J. Phys. B 10, 2767 (1977).

54. J. Simons, Ann. Rev. Phys. Chem. 28, 15 (1977).

55. F. Tsui and K. F. Freed, Chem. Phys. Lett. 32, 345 (1975).

56. K. F. Freed and D. L. Yeager, Chem. Phys. 22, 401 (1977).

57. D. L. Yeager and K. F. Freed, Chem. Phys. 22, 415 (1977).

58. J. Linderberg and Y. Ohrn, Propagators in Quantum Chemistry, (Academic, New York, 1973).

59. J. Linderberg and Y. Ohrn, Int. J. Quant. Chem. 12, 161 (1977).

60. L. S. Cederbaum, G. Hohlneicher and S. Peyerimhoff, Chem. Phys. Lett. 11, 421 (1971).

61. G. Hohlneicher, F. Ecker and L. S. Cederbaum, in Electron Spectroscopy, edited by D. A. Shirley, (North-Holland, Amsterdam, 1972), p. 647.

62. F. Ecker and G. Hohlneicher, Theor. Chim. Acta 25, 289 (1972).

63. L. S. Cederbaum, G. Hohlneicher and W. von Niessen, Chem. Phys. Lett. 18, 503 (1973).

64. L. S. Cederbaum, G. Hohlneicher and W. von Niessen, Mol. Phys. 26, 1405 (1973).

65. L. S. Cederbaum, Theor. Chim. Acta 31, 239 (1973).

66. L. S. Cederbaum and W. von Niessen, Chem. Phys. Lett. 24, 263 (1974).

67. L. S. Cederbaum, Mol. Phys. 28, 479 (1974).

68. L. S. Cederabaum, Chem. Phys. Lett. 25, 562 (1974).

69. W. von Niessen, G.H.R. Diercksen and L. S. Cederbaum, J. Chem. Phys. 67, 4124 (1977).

70. L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. 36, 205 (1977).

71. J. Schirmer and L. S. Cederbaum, J. Phys. B 11, 1889 (1978).

72. J. Oddershede and N. Flander, J. Chem. Phys. 65, 3495 (1976).

73. J. Oddershede, P. Jorgensen and N.H.F. Beebe, Int. J. Quant. Chem. 12, 655 (1977).

74. J. Oddershede and P. Jorgensen, J. Chem. Phys. 66, 1541 (1977).

75. N. Elander, J. Oddershede and N.H.F. Beebe, Astrophys. J. 216, 165 (1977).

76. J. Oddershede, P. Jorgensen and N.H.F. Beebe, J. Phys. B 11, 1 (1978).

77. J. Oddershede, Adv. Quant. Chem. 11, 275 (1978).

78. A. Banerjee, R. Shepard and J. Simons, Int. J. Quant. Chem. Symp. 12, 389 (1978).

79. A. Banerjee, J. W. Kenney and J. Simons, Int. J. Quant. Chem. 16, 1209 (1979).

80. G. Born, H. A. Kurtz and Y. J. Ohrn, J. Chem. Phys. 68, 74 (1978).

81. H. A. Kurtz and Y. J. Ohrn, J. Chem. Phys. 69, 1162 (1978).

82. G. Born and Y. Ohrn, Phys. Scrip. 21, 378 (1980).

83. B. Weiner and O. Goscinski, Int. J. Quant. Chem. 12, 299 (1977).

84. O. Goscinski and B. Weiner, Phys. Scrip. 21, 385 (1980).

85. B. Weiner and O. Goscinski, Int. J. Quant. Chem. 21, 369 (1982).

86. P. Nozieres and D. Pines, Phys. Rev. 109, 762 (1958).

87. H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

Publications and Papers

1. "Susceptibility and Dielectric Function Formulas That Are Consistent with the Hartree-Fock Approximation", N. E. Brener, Bull. Am. Phys. Soc. 28, 204 (1983).

2. "Selection of a Dielectric Function Formula That Is Consistent with the Hartree-Fock Approximation", A. Bakhshai and N. E. Brener, Bull. Am. Phys. Soc. 28, 267 (1983).

3. "Calculations of Activation Energies of Molecules", G. D. Eknayan, L. M. Holaday, A. Bakhshai, M. E. Cox and N. E. Brener, Bull. Am. Phys. Soc. 28, 307 (1983).

4. "Higher Order Correlation Terms in the Screened Exchange Plus Coulomb Hole Method", A. Bakhshai, D. Jiang and N. E. Brener, Bull. Am. Phys. Soc. 29, 46 (1984).

5. "Effect of Correlation on Molecular Electronic Structure Calculations", D. Orr, A. Bakhshai, G. D. Eknayan, L. M. Holaday, E. R. Hernandez and N. E. Brener, Bull. Am. Phys. Soc. 29, 47 (1984).

6. "MNDOC Calculations of Molecular Activation Energies", E. R. Hernandez, L. M. Holaday, R. H. Pressley, G. D. Eknayan, A. Bakhshai and N. E. Brener, Bull. Am. Phys. Soc. 29, 47 (1984).

7. "A New One-Electron Equation That Contains Second Order Correlation Terms", N. E. Brener, A. Bakhshai, D. Orr and D. Jiang, Bull. Am. Phys. Soc. 29, 351 (1984).

8. "Short Range Correlation Effects in FeO and MnO", L. M. Holaday, G. E. Moericke, A. Bakhshai, G. D. Eknayan and N. E. Brener, Bull. Am. Phys. Soc. 29, 393 (1984).

9. "Calculations of the Activation Energy of Nitromethane and Methyl Nitrite", E. R. Hernandez, L. M. Holaday, R. H. Pressley, G. D. Eknayan, A. Bakhshai and N. E. Brener, Bull. Am. Phys. Soc. 29, 399 (1984).

10. "Generalized Random Phase Approximation Formalism for the Dielectric Function", N. E. Brener and A. Bakhshai, Phys. Rev. B (submitted for publication).

11. "A New One-Electron Equation That Contains Second Order Correlation Terms", N. E. Brener and A. Bakhshai, Phys. Rev. B (submitted for publication).

12. "MNDOC Calculations of the Activation Energy of Nitromethane and Methyl Nitrite", L. M. Holaday, E. R. Hernandez, A. Bakhshai, R. H. Pressley and N. E. Brener, Chem. Phys. Lett. (submitted for publication).

13. "Configuration Interaction Calculations for Nitromethane", D. E. Orr and N. E. Brener, Bull. Am. Phys. Soc. 30 (1985).

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